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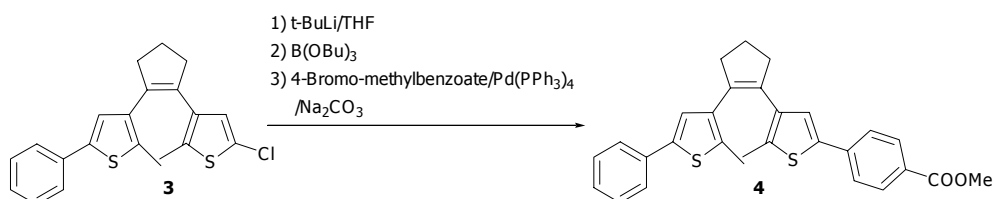
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**Photo- and Electro-chromism of Diarylethene Modified ITO Electrodes – towards
Molecular based Read-Write-Erase Information storage.**

Jetsuda Areephong, Wesley R. Browne, Nathalie Katsonis and Ben. L. Feringa*

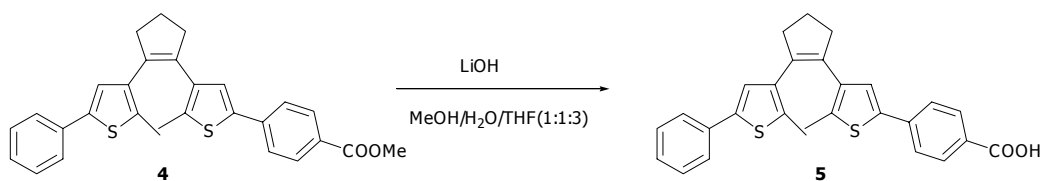
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Experimental

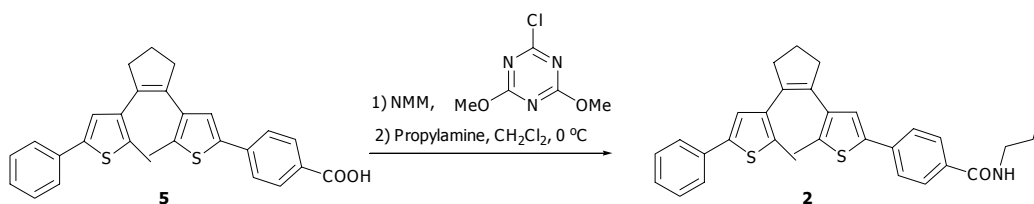


Methyl-4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoate (4). 3-(2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-enyl)-2-methyl-5-phenylthiophene **3** (0.87 g, 2.36 mmol) in THF (40 ml) was treated with *t*-BuLi (2.36 ml, 1.5 M in pentane, 3.54 mmol) under a N₂ atmosphere. After 1 h, B(OBu)₃ (0.95 ml, 3.54 mmol) was added and the mixture was stirred for 1 h at room temperature. A separate flask was charged with methyl 4-bromobenzoate (0.76 g, 3.54 mmol), [Pd(PPh₃)₄] (81 mg, 0.07 mmol), THF (50 ml), aqueous Na₂CO₃ (2 M, 10 ml) and ethylene glycol (10 drops). The mixture was heated to 80 °C and the preformed boronic ester was added slowly. The reaction mixture was heated at reflux overnight, cooled to room temperature, diluted with diethyl ether (50 ml) and washed with H₂O (50 ml). The aqueous layer was extracted with diethyl ether (50 ml). The combined organic layers were dried over Na₂SO₄. After evaporation of the solvent, the product was purified by column chromatography on silica gel (heptane) to afford **4** as a sticky oil (0.56 g, 51%). ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.02 (s, 3H), 2.10 (m, 2H), 2.85 (t, *J* = 7.34, 7.69 Hz, 4H), 3.91 (s, 3H), 7.03 (s, 1H), 7.15 (s, 1H), 7.22 (t, *J* = 7.33, 7.34 Hz, 1H), 7.33 (t, *J* = 7.33, 8.07 Hz, 2H), 7.50 (d, *J* = 7.33 Hz, 2H), 7.54 (d, *J* = 8.43 Hz, 2H), 7.99 (d, *J* = 8.80 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.43 (q), 14.54 (q), 23 (t), 38.44 (t), 38.47 (t), 52.04 (q), 123.88 (d), 124.80 (d), 125.29 (d), 125.54 (d), 126.98 (d), 128.15 (s), 128.78 (d), 130.18 (d), 134.26 (s), 134.42 (s), 134.46 (s), 135.09 (s), 136.30 (s), 136.52 (s), 137.11 (s), 138.29 (s), 138.73 (s),

139.79 (s), 166.79 (s). EI-MS (m/z): 470 (M^+ , 100); HRMS calcd for $C_{29}H_{26}O_2S_2$ 470.1374, found 470.1399.

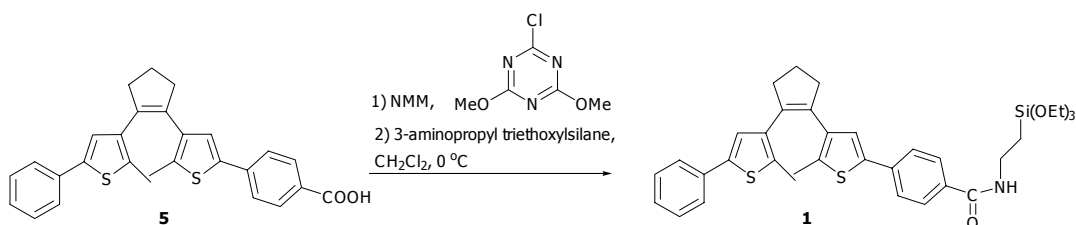


4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoic acid (5). Methyl-4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoate (**4**) (0.56 g, 1.21 mmol) and LiOH (0.15 g, 6 mmol) was added to 50 mL of MeOH/H₂O/THF (1:1:3 v/v/v). The suspension was stirred at room temperature for 10 h. The mixture was acidified carefully by dropwise addition of 2 M aq. HCl. The aqueous layer was extracted with dichloromethane (3x50 ml). The combined organic layer was washed with sat. aq. NaCl, dried over Na₂SO₄, and the solvent removed *in vacuo*. The product was recrystallized from dichloromethane/methanol, to yield compound **5** as a brown solid (0.49 g, 89%). ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.03 (s, 3H), 2.10 (m, 2H), 2.86 (t, J = 7.34, 7.33 Hz, 4H), 7.03 (s, 1H), 7.18 (s, 1H), 7.23 (m, 1H), 7.33 (t, J = 7.70, 7.33 Hz, 2H), 7.50 (d, J = 7.70 Hz, 2H), 7.58 (d, J = 8.43 Hz, 2H), 8.06 (d, J = 8.70 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.43 (q), 14.57 (q), 23.00 (t), 38.44 (t), 38.48 (t), 123.87 (d), 124.87 (d), 125.29 (d), 125.85 (d), 126.99 (d), 127.13 (s), 128.78 (d), 130.84 (d), 134.21 (s), 134.41 (s), 134.47 (s), 135.18 (s), 136.50 (s), 136.65 (s), 137.20 (s), 138.15 (s), 139.59 (s), 139.82 (s), 171.36 (s). EI-MS (m/z): 456 (M^+ , 100); HRMS calcd. for $C_{28}H_{24}O_2S_2$ 456.121, found 456.120. M.P. 170.7-171.7 °C.



4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)-N-propylbenzamide (2). 4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoic acid (**5**) (100 mg, 0.22 mmol) was suspended in CH₂Cl₂ (5 ml) and placed in ice bath. Subsequently N-

methylmorpholine (30 μ l, 0.22 mmol) was added and the compound dissolved. Next 2-chloro-4,6-dimethoxytriazine (46 mg, 0.22 mmol) was added. The reaction mixture was stirred for 2 h at 0 $^{\circ}$ C, and a second equivalent of N-methylmorpholine (30 μ l, 0.22 mmol) was added followed by propylamine (43 μ l, 0.44 mmol). Stirring was continued for 1 h at 0 $^{\circ}$ C, and subsequently overnight at room temperature. CH_2Cl_2 (50 ml) was added and the solution was washed with, respectively, 1M aq. HCl (2 x 20 ml), brine (1 x 20 ml), saturated aqueous bicarbonate solution (1x20 ml) and H_2O (1x20 ml). The organic phase was dried over Na_2SO_4 and after evaporation of the solvent a solid was obtained. After purification by column chromatography (EtOAc/heptane = 5:95) a brown solid was obtained (48 mg, 43%). ^1H NMR (400 MHz, CDCl_3) δ 0.98 (t, J = 7.33, 7.70 Hz, 3H), 1.64 (m, 2H), 2.00 (s, 3H), 2.02 (s, 3H), 2.09 (m, 2H), 2.85 (t, J = 7.70, 7.33 Hz, 4H), 3.41 (m, 2H), 6.15 (br, 1H), 7.03 (s, 1H), 7.10 (s, 1H), 7.22 (m, 1H), 7.33 (t, J = 7.33, 7.70 Hz, 2H), 7.50 (d, J = 6.97 Hz, 2H), 7.53 (d, J = 8.43 Hz, 2H), 7.72 (d, J = 8.43 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.42 (q), 14.00 (q), 14.49 (q), 22.93 (t), 23.00 (t), 38.41 (t), 38.49 (t), 41.74 (t), 123.90 (d), 125.04 (d), 125.15 (d), 125.28 (d), 126.95 (d), 127.40 (d), 128.45 (d), 128.75 (d), 131.71 (d), 132.79 (s), 134.33 (s), 134.43 (s), 134.46 (s), 135.01 (s), 135.81 (s), 136.54 (s), 136.99 (s), 137.32 (s), 138.32 (s), 139.74 (s), 166.94 (s). EI-MS (m/z): 497 (M^+ , 100); HRMS calcd for $\text{C}_{31}\text{H}_{31}\text{NOS}_2$ 497.185, found 497.184. M.P. 78-79 $^{\circ}$ C.



4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)-N-(2-(triethoxysilyl)ethyl)benzamide (1). 4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoic acid (**5**) (100 mg, 0.23 mmol) was suspended in CH_2Cl_2 (5 ml) and placed in ice bath. Subsequently N-methylmorpholine (25 ml, 0.23 mmol) was added suspension became a solution. Then 2-chloro-4,6-dimethoxytriazine (40 mg, 0.23 mmol) was added. The reaction mixture was stirred for 2 h at 0 $^{\circ}$ C, and a second equivalent of N-methylmorpholine (25 ml, 0.23 mmol) was added followed by n-aminopropyltriethoxysilane (0.16 ml, 0.69

mmol). Stirring was continued for 1 h at 0 °C, and overnight at room temperature. The reaction mixture was filtered and solvent removed in vacuo. The product was purified by flash column chromatography (1:1 EtOAc : Heptane) a sticky oil was obtained (0.11 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ 0.70 (m, 2H), 1.22 (m, 9H), 1.75 (m, 2H), 1.99 (s, 3H), 2.00 (s, 3H), 2.08 (m, 2H), 2.86 (m, 4H), 3.45 (m, 2H), 3.83 (m, 6H), 6.51 (br, 1H), 7.03 (s, 1H), 7.10 (s, 1H), 7.23 (m, 1H), 7.32 (t, *J*=7.33, 7.79 Hz, 2H), 7.51 (m, 4H), 7.73 (d, *J*=8.43 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 7.78 (t), 14.40 (q), 14.49 (q), 18.25 (q), 22.74 (t), 22.84 (t), 38.41 (t), 38.44 (t), 42.17 (t), 58.49 (t), 123.88 (d), 124.98 (d), 125.09 (d), 125.26 (d), 126.95 (d), 127.45 (d), 128.52 (d), 128.75 (d), 131.64 (d), 132.83 (s), 134.33 (s), 134.41 (s), 134.45 (s), 134.97 (s), 135.76 (s), 136.55 (s), 136.97 (s), 137.24 (s), 138.37 (s), 139.73 (s), 166.88 (s). EI-MS (*m/z*): 659 (*M*⁺, 100); HRMS calcd for C₃₄H₄₅NO₄S₂Si 659.256, found 659.257.

Electrode Modification

The ITO glass slides were treated with a 1 mM solution of compound **1** at reflux in dry toluene for 24 h. The modified ITO samples were then washed with HPLC-grade toluene, HPLC-grade methanol and HPLC grade *iso*-propanol and dried with the stream of nitrogen.

Electrochemistry

Electrochemical measurements were carried out on a Model 630B Electrochemical Workstation (CHInstruments) using a saturated calomel reference electrode (SCE) and Pt wire as auxiliary electrode. The working electrodes were ITO-coated glass slides (Prazisions Glas & Optik GmbH, Germany) or glassy carbon electrodes in the case of **2o/2c**. The supporting electrolytes were n-Bu₄NPF₆ (TBAP) and n-TBA(CF₃SO₃) 0.1 M in CH₂Cl₂.

Cyclic voltammetry of ITO glass before and after activation

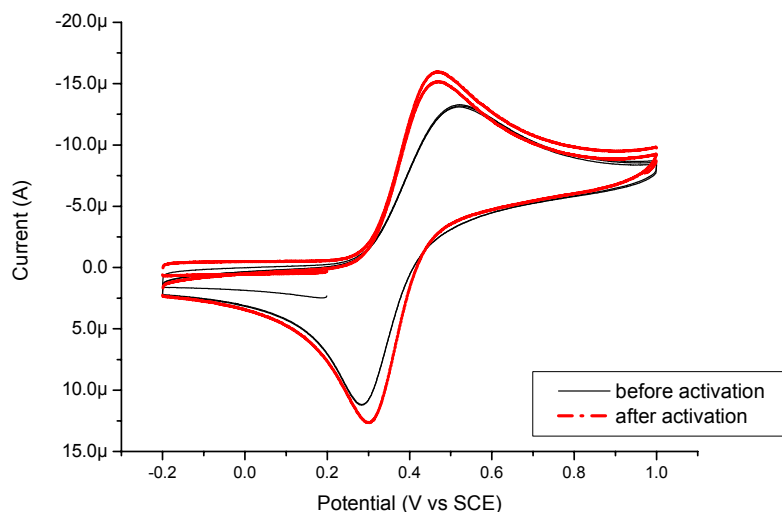


Figure S1. Cyclic voltammogram of Ferrocene in 0.1 M TBAP/CH₃CN recorded with ITO electrodes at the scan rate of 0.1 Vs⁻¹. Solid line, ITO before activation with basic H₂O₂ solution; dotted line, ITO after activation with basic H₂O₂ solution.

Surface roughness determination

A Dimension scanning probe microscope (Digital Instruments) was employed to observe the film morphology. The characterization was performed under ambient conditions by tapping mode AFM on several samples of **1o-ITO** and with different tips. The root mean square (RMS) surface roughness of the surface of **1o-ITO** as measured by atomic force microscopy (AFM) on areas typically of 1x1 μm² was 12 nm. For Figure S2a, the effective area was calculated to be 0.7764 μm² by WsXM software, which corresponds to a roughness factor of 1.2. AFM phase contrast images have been shown to be sensitive to material surface properties, such as chemical composition. Figure S2b is the phase contrast image corresponding to the topography shown on Figure S2a. It shows a different contrast than Figure S2a. This contrast corresponds to uncovered or monolayer-covered ITO areas. It shows that the organic coverage is homogeneously distributed over the surface.

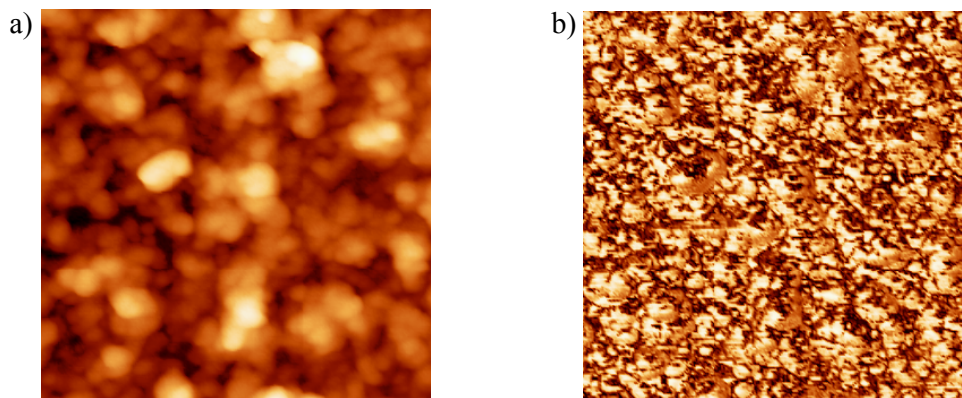


Figure S2. AFM images of the monolayer/ITO surface. Scale: $0.8 \times 0.8 \mu\text{m}^2$. a) Topographic image b) Phase contrast image.

Cyclic voltammetry of **1o**-ITO

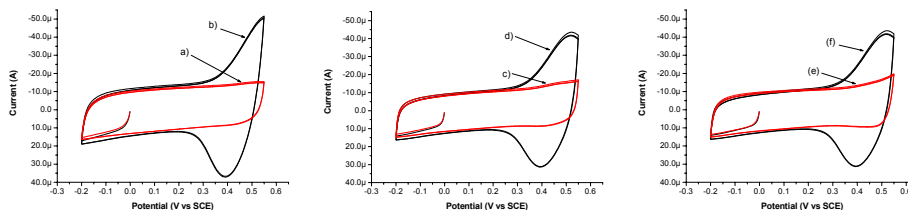


Figure S3 Photoswitching of **1o**-ITO, upon irradiation at 312 nm, and subsequently with $>400 \text{ nm}$. a) **1o**-ITO, b) after 312 nm irradiation of, c) after $>400 \text{ nm}$ irradiation, d) after 312 nm irradiation, e) after $>400 \text{ nm}$ irradiation f) after 312 nm irradiation, in 0.1 M TBA(CF_3SO_3)/ CH_2Cl_2 at scan rate 2 V s^{-1}

Electrochemical conversion of **1c**-ITO to **1o**-ITO, oxidative ring-opening

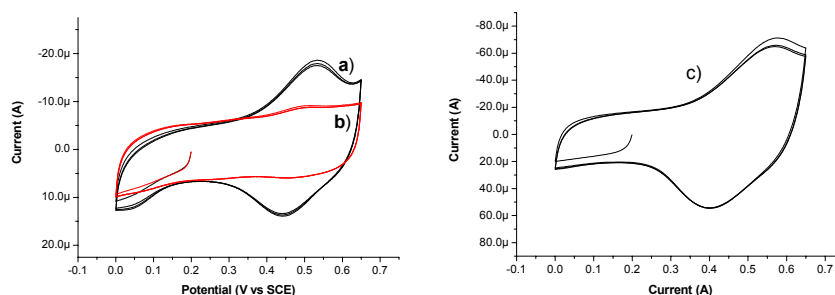


Figure S4 Cyclic voltammetry of a) **1c**-ITO (formed from **1o**-ITO by irradiation with 312 nm light); b) **1o**-ITO (after oxidative ring opening achieved by repetitive cyclic voltammetry between 0.0 and 0.6 V at 0.1 V s^{-1}) in 0.1M TBA(CF_3SO_3)/ CH_2Cl_2 at scan 0.5 Vs^{-1} and c) after irradiation of oxidatively opened **1c**-ITO with 312 nm light in 0.1 M TBA(CF_3SO_3)/ CH_2Cl_2 at scan rate 2 Vs^{-1} .

Ring opening (oxidatively) is a thermodynamically disfavoured process. It occurs through disproportionation of the monocation of the closed form **1c**⁺-ITO to the neutral compound e.g. **1c**-ITO and the dication **1c**²⁺-ITO. The dication **1c**²⁺-ITO is in equilibrium with **1o**²⁺-ITO albeit with the closed form highly favoured. In addition the dications **1c**²⁺-ITO and **1o**²⁺-ITO will undergo rapid electrochemical reduction to the monocation **1c**⁺-ITO and neutral **1o**-ITO compounds, respectively at below 0.6 V. although statistically unlikely, once ring opening does occur it is irreversible under the limited scanning range of 0-0.5 V. Hence, at high scan rates ($> 1 \text{ V s}^{-1}$) the extent of disproportion of the monocation generated is low and the rapid reduction of the dication inhibits ring opening. At slower scan rates the equilibrium is driven towards the open form **1o**-ITO, and overall ring open will be observed.

Cyclic voltammetry of **1o**-ITO before and after photochemical ring-opening followed by photochemical ring closure monitored at 0.1 V s^{-1} .

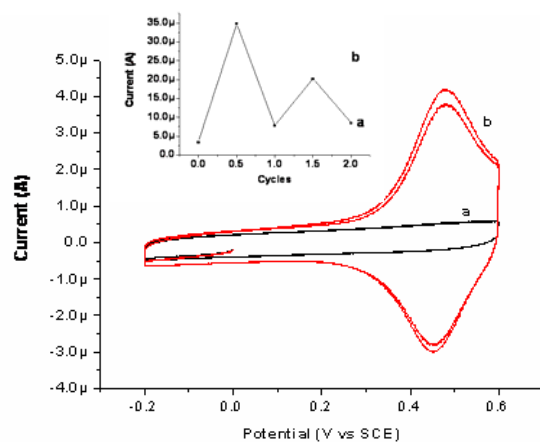


Figure S5 Cyclic voltammetry of a) **1o-ITO** and b) **1c-ITO** after irradiation at 312 nm for 5 min. Inset: Repetitive photochemical switching of **1o-ITO** to **1c-ITO**. Data recorded in 0.1 M TBAPF₆/CH₂Cl₂ at scan rate 0.1 V s⁻¹.